

## The Acid Dissociation Constants of Thioglycollic Acid

WALTER LUND and EINAR JACOBSEN

*Kjemisk Institutt A, Universitetet i Oslo, Blindern, Oslo 3, Norway*

During an investigation of some metal complexes with thioglycollic acid it was necessary to know the dissociation constants of the acid at 25 and 60°C. A literature survey showed that the constants at 60°C have not previously been determined. The constants at 25°C have been reported by several workers,<sup>1-6</sup> but different ionic strength and medium have been used, and in some cases it is quite uncertain whether the constant  $K_C$  or  $K_B$  has been determined. Recently Leussing *et al.*<sup>7-8</sup> determined the dissociation constants of the acid in 0.1 M potassium chloride at several temperatures in the range 0–40°C. The authors point out, however, that the value of  $K_1$  at 25°C ( $K_{B1} = 3.3 \times 10^{-4}$ ) appears to be too high. It was therefore decided also to redetermine the dissociation constants at 25°C.

Thioglycollic acid was obtained from E. Merck AG, Germany, and it was purified and standardized as described by Leussing and Kolthoff.<sup>4</sup> The dissociation constants were determined by potentiometric titration of  $2 \times 10^{-2}$  M thioglycollic acid in the presence of 0.1 M potassium chloride using carbonate-free potassium hydroxide as a titrant. The titrations were performed in a water-jacketed cell and the temperature was kept constant  $\pm 0.2^\circ$  by means of a thermostat and a circulating pump. The pH of the solutions was measured with a Beckman Zeromatic pH-meter. The glass and saturated calomel electrodes were standardized at each temperature against a 0.05 M potassium hydrogen *o*-phthalate buffer and against 0.01 M borax. The pH values of these standard buffers at 25 and 60°C are given by Bower and Bates.<sup>9</sup>

The Brönsted dissociation constants,<sup>10,11</sup>  $K_B$ , were calculated from the titration curves as described by Chaberek and Martell,<sup>12</sup> and the following values were obtained:

$$\begin{array}{l} 25^\circ\text{C} \quad K_{B1} = 2.8 \times 10^{-4} \quad (\text{p}K_1 = 3.55), \\ \quad \quad K_{B2} = 6.0 \times 10^{-11} \quad (\text{p}K_2 = 10.22), \\ 60^\circ\text{C} \quad K_{B1} = 2.5 \times 10^{-4} \quad (\text{p}K_1 = 3.60), \\ \quad \quad K_{B2} = 18 \times 10^{-11} \quad (\text{p}K_2 = 9.74). \end{array}$$

The Brönsted constants were converted to concentration constants using the activity coefficient of hydrogen ion equal to 0.81 and 0.78 at 25 and 60°C, respectively. The activity coefficients were calculated from the mean ionic activity coefficient of hydrochloric acid in 0.1 M potassium chloride as described by Bates.<sup>13</sup> The mean ionic activity coefficients have been determined by Harned *et al.*<sup>14-16</sup> The concentration dissociation constants,  $K_C$ , were calculated to be:

$$\begin{array}{l} 25^\circ\text{C} \quad K_{C1} = 3.6 \times 10^{-4} \quad (\text{p}K_1 = 3.45), \\ \quad \quad K_{C2} = 7.6 \times 10^{-11} \quad (\text{p}K_2 = 10.12), \\ 60^\circ\text{C} \quad K_{C1} = 3.3 \times 10^{-4} \quad (\text{p}K_1 = 3.48), \\ \quad \quad K_{C2} = 24 \times 10^{-11} \quad (\text{p}K_2 = 9.62). \end{array}$$

The present value of  $K_{B2}$  at 25°C is in good agreement with that one reported by Leussing *et al.*,<sup>8</sup> and the value of  $K_{B1}$ , which is somewhat lower than the previously published value, compares favourably with the values reported at other temperatures.<sup>8</sup>

- Ostwald, W. *Z. physik. Chem.* **3** (1889) 182.
- Klason, P. and Carlson, T. *Ber.* **39** (1906) 732.
- Larsson, E. *Z. anorg. Chem.* **172** (1928) 375.
- Leussing, D. L. and Kolthoff, I. M. *J. Electrochem. Soc.* **100** (1953) 334.
- Li, N. C. and Manning, R. A. *J. Am. Chem. Soc.* **77** (1955) 5225.
- Benesch, R. E. and Benesch, R. *J. Am. Chem. Soc.* **77** (1955) 5877.
- Leussing, D. L. *J. Am. Chem. Soc.* **80** (1958) 4180.
- Leussing, D. L., Laramy, R. E. and Alberts, G. S. *J. Am. Chem. Soc.* **82** (1960) 4826.
- Bower, V. E. and Bates, R. G. *J. Res. Natl. Bur. Std.* **59** (1957) 261.
- Brönsted, J. N. *Chem. Rev.* **5** (1928) 293.
- Rosotti, F. J. C. and Rosotti, H. *The Determination of Stability Constants*, McGraw-Hill Book Co., New York 1961, p. 8.
- Chaberek, S. and Martell, A. E. *J. Am. Chem. Soc.* **74** (1952) 5052.
- Bates, R. G. *Determination of pH, Theory and Practice*, John Wiley and Sons, New York 1964, p. 42.
- Harned, H. S. and Hamer, W. J. *J. Am. Chem. Soc.* **55** (1933) 2194.
- Harned, H. S. and Cook, M. A. *J. Am. Chem. Soc.* **59** (1937) 1290.
- Harned, H. S. and Owen, B. B. *The Physical Chemistry of Electrolytic Solutions*, Reinhold Publishing Corp., New York 1950, p. 558.

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